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(71)Applicant : SHINAGAWA REFRACT CO LTD

(72)Inventor : YAMAMURA TAKASHI
NAKAMURA RYOSUKE
UENO AKIRA

(54) COLD CURING MONOLITHIC REFRactories

(57)Abstract:

PURPOSE: To obtain the cold curing monolithic refractories having excellent workability, storage stability of a powder part, etc., by previously mixing the powders of a refractory material and sulfamic acid which is a hardener and adding a resol type phenolic resin liquid to the mixture at the time of use on site.

CONSTITUTION: The powder part is produced by mixing 0.01 to 10 pts.wt. sulfamic acid into 100 pts.wt. refractory material (e.g.; magnesia). The granular sulfamic acid having about 0.07 to 1mm average grain sizes is preferable as the sulfamic acid to be added. This powder part and the resol type phenolic resin liquid which is the binder are mixed on use site and the mixture is kneaded, by which the cold curing monolithic refractories are produced and applied. The amt. of the resol type phenolic resin liquid to be used is adequately about 3.5 to 20 pts.wt. per 100 pts.wt. refractory material in the powder part. As a result, an abrupt curing reaction does not take place at the time of kneading of the powder part and the resin liquid part and, therefore, the stable application is made possible.

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CLAIMS

[Claim(s)]

[Claim 1] Room-temperature-setting nature unshaped refractories which consist of the fine-particles section and resol type phenol resin liquid which consist of fire-resisting material and a sulfamic acid.

[Claim 2] Room-temperature-setting nature unshaped refractories according to claim 1 whose sulfamic-acid addition to the fire-resisting-material 100 weight section is 0.01 weight section - 10 weight section.

[Claim 3] Room-temperature-setting nature unshaped refractories according to claim 1 whose resol type phenol resin liquid is 3.5 weight sections - 20 weight section to the fire-resisting-material 100 weight section.

[Claim 4] Room-temperature-setting nature unshaped refractories according to claim 1 whose mean particle diameter of a sulfamic acid is 0.07mm - 1mm.

[Claim 5] Room-temperature-setting nature unshaped refractories according to claim 1 which contain a magnesium oxide more than 2 weight sections in the fire-resisting-material 100 weight section.

[Claim 6] Operation of the room-temperature-setting nature unshaped refractories characterized by blending dryly beforehand the sulfamic acid and fire-resisting material which are a powder-like in solid form, mixing and kneading this mixture and resol type phenol resin liquid in a use site, and constructing.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] The room-temperature-setting nature unshaped refractories of this invention are used for lining, lining lining, and repair of the oven used under the elevated temperature of objects for iron manufacture, such as *****, a mixer car, a ladle, convertor, an electric furnace, vacuum-degassing equipment, and tundish, and others.

[0002]

[Description of the Prior Art] The refractories in which use tar, a pitch, and various resins and carbon bond is made to form by heating have the feature excellent in the field of a spalling resistance or a warm strength, and are widely used by various ovens in recent years.

[0003] Phenol resin is widely used for the unshaped refractories of the type which forms carbon bond by heating as a binder. In order to make phenol resin into a binder and to give room-temperature-setting nature, combination with various curing agents is proposed.

[0004] Generally, it uses for resol type phenol resin by learning widely the room-temperature-setting method called so-called acid hardening which adds strong acid, such as Para toluenesulfonic acid, a benzenesulfonic acid, a xylene sulfonic acid, a sulfuric acid, and phosphoric acid. However, like refractories, since the irritating odor is strong, when about dozens of t constructs at once, practical use on environment is difficult for Para toluenesulfonic acid etc. On the other hand, since inorganic acids, such as a sulfuric acid, are added with a liquid, local hardening with resin liquid arises, or they have problems, like a working life becomes short. Furthermore, when the basic aggregate is used in the case of refractories, the acid and the basic aggregate of a liquid may carry out a direct reaction, and may produce variation in the hardenability of a resin.

[0005] Moreover, although there is a method of making phenol resin add and harden the poly isocyanate, in using for the basic fireproof aggregate, for example, basic fire-resisting material works as a hardening accelerator of the poly isocyanate, it hardens during kneading or there are problems, like a working life becomes extremely short.

[0006] Various curing agents are proposed as the new room-temperature-setting method which changes to such a room-temperature-setting method. For example, in order to carry out room temperature setting of the thermosetting resin, adding lactone and lactams is proposed by JP,58-20771,A and JP,58-69782,A. Although it is possible to give room-temperature-setting nature by adding these also to alkaline water-soluble resol type phenol resin, these curing agents are liquids, and since they carry out a hardening start shortly after mixing with resol type phenol resin liquid,

they cannot mix two kinds of liquid beforehand. Therefore, in mixture, it is necessary to mix three sorts of curing agent liquid with fire-resisting material and liquid phenol resin by the specific ratio, and further, in order to adjust the setting time, you have to carry out suitable amount addition mixture of the alkali. Thus, in order to have to add and knead how many kind thing material, not only work is complicated, but there is a fault of being easy to produce variation in the workability and hardenability of a kneading object according to the addition error of each quantitative ratio.

[0007] Moreover, although using a hydroxy acid, amino acid, and amides is proposed by JP,59-137370,A as a curing agent of a resin, by this method, the intensity after hardening of a resin is not enough, the phenomenon which some resins soften and carries out huge during heating in the time of being used as refractories is seen, and there is a fault that construction volume density falls remarkably.

[0008]

[Problem(s) to be Solved by the Invention] thus, the method that good room-temperature-setting nature is given to the unshaped refractories which made phenol resin the binder, and the setting time can be adjusted to them is hard to be referred to as being established practical, and it is necessary to use it, combining the various additives containing a curing agent intricately, and on the other hand, when adjustment is easy, the hardening itself is inadequate [the method] -- etc. -- there was a problem

[0009] this invention is made in order to solve such a trouble, and adjustment of the setting time is very easy for it, and it offers the room-temperature-setting nature which was moreover excellent, and unshaped refractories with the intensity after hardening.

[0010]

[Means for Solving the Problem] In the unshaped refractories which used phenol resin as a main binder in order to obtain a firm carbon connective tissue by heating The result which examined many things about the curing agent for making it harden by ordinary temperature care of health after constructing in ordinary temperature, By blending dryly beforehand with fire-resisting material the sulfamic acid which is a powder-like in solid form, and mixing and kneading resol type phenol resin liquid in a use site at this It found out that the setting time could be arbitrarily adjusted only by being able to obtain good room-temperature-setting nature, and making the amount of the sulfamic acid used fluctuate, and resulted in this invention. this invention is explained in full detail below.

[0011] Acidity and various neutral and basic fireproof material are applicable to the fire-resisting material used for this invention. For the use which the kind of refractory material should be chosen by the service condition of the oven used, and is exposed to slags with comparatively powerful acidity, such as ***** and a mixer car acidity [, such as SiO₂, ZrO₂, aluminum 2O₃, and SiC,] - a neutral refractory material -- good -- on the other hand -- the comparatively high slag of the basicity of a converter, an electric furnace, etc. -- receiving -- MgO, CaO, aluminum 2O₃, and Cr 2O₃ etc. -- basic - a neutral fire-resisting material is suitable In addition, although the nature material of carbon may not necessarily be called fire-resisting material, using slag-proof infiltrative or the property of high temperature conductivity, in recent years, it is widely used for refractories and, naturally it should be considered also in the unshaped refractories of this invention that it is a kind of fire-resisting material.

[0012] Moreover, it should be adjusted and such fire-resisting material should be used so that it may become the suitable grain-size composition according to each construction method of unshaped refractories. For example, in for casting construction, it may be common to think a fluidity as important and to consider as the continuation grain size to a coarse-grain - fines region, and the particle size blending which added superfines for improvement in a fluid improvement and restoration nature may also be required for it. As other construction methods, although there are a stamp, spraying, trowel coating, pressing fit, etc., it is desirable to use the fire-resisting material which performed grain refining in consideration of each workability and restoration nature.

[0013] A sulfamic acid must contain in the fine-particles section which constitutes the unshaped refractories of this invention. A sulfamic acid is N-alkyl [which is expressed with R2 NSO₃ H], N-aryl derivative, or NH₂ SO₃ H.

[0014] It is a transparent and colorless non-hygroscopic crystalline, and in an ordinary temperature air, since NH₂ SO₃ H is a stable solid-state, it does not have an odor, either and is easy handling. NH₂ SO₃ H shows the strong acid nature not more than pH=1.0 in about 2% of solution. Paying attention to the stability and strong acid nature of such a sulfamic acid, this invention persons examine many things and result in this invention.

[0015] Since a sulfamic acid is stable in an ordinary temperature air and does not have hygroscopicity, either, powder and the fine-particles section which was granular, could deal with and was mixed with fire-resisting material are excellent also in storage stability on a par with fire-resisting material. On the other hand, if resol type phenol resin liquid is added and kneaded in this fine-particles section in a construction site, a sulfamic acid will express the property of strong acid, will react with resin liquid gradually, and will carry out room temperature setting of the resin.

[0016] Therefore, in the room-temperature-setting nature unshaped refractories of this invention, construction in a

use site can be used only by mixing and kneading one kind of liquid which replaces the fine-particles section and water like the unshaped refractories using conventional water. A sulfamic acid is a solid-state, and since it does not react rapidly like [in the case of the curing agent of a liquid] even if it mixes and kneads with resol type phenol resin liquid, construction workability is not checked.

[0017] Here, it mainly depends for the reactivity of resol type phenol resin liquid and a sulfamic acid on the addition of a sulfamic acid. That is, if there are few sulfamic-acid additions, the setting time will become long, and if an addition is made to increase conversely, it will harden for a short time. Moreover, the reactivity of resol type phenol resin liquid and a sulfamic acid receives influence also in temperature. If atmospheric temperature is high, the setting time of the increase of reactivity and a construction object will become short, and the setting time will become long under low temperature.

[0018] therefore, depending on operation, when the setting time of about 1 law needs to be set up through every year To adjust so that hardening may not arise when constructing a lot of [conversely] refractories to harden especially in a short time until construction is finally completed Adjustment of the setting time is easily possible and it is not necessary to add other additives further like before only by fluctuating the amount of sulfamic acids in the fine-particles section.

[0019] As for the addition of a sulfamic acid, it is desirable that it is in 0.01 weight sections - 10 weight section to the fire-resisting-material 100 weight section. That is, the case where hardening of a resin became imperfect was seen at the 0.01 weight sections end. On the contrary, since a working life will also become short at the same time the setting time is shortened if it adds exceeding 10 weight sections, after kneading the fine-particles section and resol type phenol resin liquid, construction must be finished for a short time and it cannot be said that it is desirable practically. Within the limits of 0.01 weight section - 10 weight section, adjustment of the setting time is possible.

[0020] Moreover, the sulfamic acid added in the fine-particles section of this invention has that desirable whose mean particle diameter is 0.07mm - about 1mm. Since reactivity will become high if atmospheric temperature is high, when the mean particle diameter was small, and was too finer than 0.07mm and it kneads with resol type phenol resin liquid and change of the setting time will become large too much with few [an addition] errors if it is going to adjust the setting time by the change in a sulfamic-acid addition, it is not desirable. On the other hand, when a sulfamic acid consists of a coarse grain exceeding 1mm of mean particle diameters, degree of dispersion in material is hard to be called homogeneity, and is not desirable. It is in the range whose mean particle diameter is 0.1mm - 0.8mm most preferably, and 50% or less of thing has the good content of powder finer than 0.07mm.

[0021] There is especially no limitation in the resol type phenol resin liquid used for the room-temperature-setting nature unshaped refractories of this invention, and it can use the thing of the grade generally marketed for it. Resol type phenol resin is usually a liquid. What added and mixed various solvents further and adjusted viscosity to this is usable.

[0022] Two roles are imposed on the resol type phenol resin liquid used for the unshaped refractories of this invention. One is the duty of the liquid as a substitute of the water used by the conventional unshaped refractories, and another is an effect as a binder demonstrated by the pitch.

[0023] Therefore, the amount of mixtures of the resol type phenol resin liquid in the unshaped refractories of this invention must be determined from both sides of the amount as a liquid required like water to give workability and restoration nature, and the amount for demonstrating sufficient bonding strength as a binder. The amount as a binder is the field of the amount of carbon bond generation after being heated, and it can be said that more ones are desirable. However, more than the 3.5 weight sections of the proper amount as a liquid are good below 20 weight sections to the fire-resisting-material 100 weight section. That is, when exceeding 20 weight sections, after being constructed, with volatilization of a solvent in the process used under an elevated temperature, and disassembly of a resin, elevation of the porosity of a construction object will become large and restoration nature will be reduced. On the other hand, since the restoration nature at the time of construction falls that they are under the 3.5 weight sections, it is not desirable.

[0024] Although acidity and various neutral and basic fire-resisting material are applicable to the fire-resisting material used for this invention as mentioned above, the intensity after hardening can be raised by making the magnesium oxide more than 2 weight sections contain here. The effect does not appear not much notably under in 2 weight sections. On the other hand, when adding so much, it should be determined in consideration of the difference of an expansion property under affinity with fire-resisting material, i.e., heating process, and an elevated-temperature state, the melting point of the volume change by the reaction, or a product, slag-proof erosion nature, etc. Therefore, the amount of mixtures of a magnesium oxide is more than 2 weight sections, and a peak is changed according to the kind of fire-resisting material.

[0025] In addition, in order to improve the wettability of fire-resisting material and resol type phenol resin liquid to the unshaped refractories of this invention or to raise the dispersibility of fines to them, it is possible to add a little

surfactant, in order [furthermore,] to stabilize the carbon bond by carbonization of the resin after heating or to raise a warm strength -- a metal powder or alloy powders, such as aluminum, Si, and Mg, and B₄C and CaB₆ etc. -- a boride, carbide, etc. can also be added

[0026]

[Example] Unshaped refractories as shown in the following table 1 were created using the magnesia clinker of 98% of MgO contents as a fire-resisting material, and each working life, the setting time, and the intensity after hardening were measured. In the examples 1, 2, 3, and 4 of this invention, the sulfamic-acid (NH₂SO₃H) addition of 0.5mm of mean particle diameters was changed from the 0.05 weight section to 3 weight sections, the fine-particles section mixed with magnesia fire-resisting material, respectively was prepared, the resol type phenol resin liquid 12 weight section was added to this, it kneaded by the small mixer, and casting material was created.

[0027] In the example A of comparison, although gamma-butyrolactone was used as a curing agent, since gamma-butyrolactone was a liquid, it kneaded by supplying to a mixer simultaneous [magnesia fire-resisting material, resol type phenol resin liquid and three sorts of gamma-butyrolactone].

[0028] Since the curing agent acetamides of the example B of comparison were fine particles, they were kneaded in the same procedure as the example of this invention. However, the amount of resol type phenol resin was made into 18 weight sections in order to secure a fluidity.

[0029] 1.5kg was first taken for these casting material on the ball as an object for working-life measurement, and 1kg was sealed and left in the plastic bag in setting-time measurement, and it slushed into two 40x40x160mm mold as an object for after [hardening] on-the-strength measurement, and fabricated.

[0030] A working life takes the sample in a ball to a flow cone, and is JIS. According to R-2521, the flow value was measured at intervals of 15 minutes, and time until the use as casting material is set to 125mm or less which is a difficult flow value was expressed as a working life. The setting time was made into time until a graduation shows 80 or more using a GHT type hardness meter timely from a plastic bag top. Three-point flexural strength was measured for each casting sample after the regimen one whole day and night, and the two averages were made into the intensity after hardening. In addition, the exam was carried out at the room temperature of 20 degrees C - 25 degrees C.

[0031]

[Table 1]

	本発明例				比較例	
	1	2	3	4	A	B
耐火材料 種類 重量部	マグネシア 100	マグネシア 100	マグネシア 100	マグネシア 100	マグネシア 100	マグネシア 100
レリーフ型 フェノール樹脂量	12	12	12	12	12	18
スルファミン酸量	0.05	0.2	0.8	3	—	—
γ-ブチロラクトン量 アセトアミド量	—	—	—	—	8	2
施工方法	流し込み	流し込み	流し込み	流し込み	流し込み	流し込み
可使時間 (時間)	6	4	1.5	0.5	2.5	3.5
硬化時間 (時間)	20	12	4.5	1.5	18	24
硬化後強度 (Mpa)	0.9	1.0	0.8	0.8	0.5	0.2

[0032]
[Table 2]

	本発明例			
	5	6	7	8
耐火材料 アルミナ カーボン 酸化マグネシウム	95 5 0	93 5 2	90 5 5	85 5 10
レジン型フェノール 樹脂	11	11	11	4
スルファミン酸	0.3	0.3	0.3	0.1
施工方法	流し込み	流し込み	流し込み	振動加圧
可使時間 (時間)	3.5	3	3	2
硬化時間 (時間)	10	9	9	7
硬化後強度 (Mpa)	0.6	1.1	1.3	1.6

[0033] In the example of this invention, by changing a sulfamic-acid addition shows that it is easy to change the setting time so that clearly from Table 1. In addition, practically, although the one where a working life is longer tends to use the setting time even if it is short, if the setting time is generally shortened with a natural thing, a working life will also become short here. although the example of this invention is not an exception, either, if it compares with the example of comparison -- the setting time of the same grade -- a working life -- a double-precision grade -- it can be said that it is long and is the material which is easy to use it If a working life will be taken into consideration even if in other words it adds other hardening regulators in the case of the example of comparison, the room which can shorten the setting time not much can be said that there is nothing. The example of this invention indicates about about 2-time intensity to be 0.8Mpa-1.0Mpa to the examples of comparison of the intensity after hardening being 0.5Mpa and 0.2Mpa.

[0034] In the example of this invention, the effect of the improvement after hardening in on the strength by addition of a magnesium oxide is expressed to Table 2. The amount of magnesium oxides was changed using aluminum₂O₃ 85% of an alumina raw material and carbon as a fire-resisting material.

[0035] 11% of resol type phenol resin liquid and 0.3% of sulfamic acids were used for the examples 5, 6, and 7 of this invention as an object for casting construction, and they made the example 8 of this invention 4% of resol type phenol resin liquid, and 0.1% of sulfamic acids as an object for oscillating pressing. Although there is no big difference in a working life and the setting time at three sorts of casting material, as for the intensity after hardening, improving is distinct as the amount of mixtures of a magnesium oxide increases. Moreover, an oscillating pressing article has little resin volume, and since it is applying the pressure at the time of fabrication, restoration nature is good, the effect of a magnesium oxide is promoted, and it shows the highest intensity after hardening.

[0036]

[Effect of the Invention] The room-temperature-setting nature unshaped refractories of this invention are use sites, and the simple kneading work of only two persons of the fine-particles section and a resin liquid part of them can be attained, and they can improve the storage stability of the fine-particles section. Moreover, since a rapid hardening reaction does not arise at the time of kneading with the fine-particles section and a resin liquid part, a working life is comparatively long, and since the stable construction is attained and it becomes possible further to adjust the setting time freely only by changing the sulfamic-acid addition which is a curing agent, other hardening regulators do not

need. Moreover, the high construction object of the intensity after hardening can be acquired.